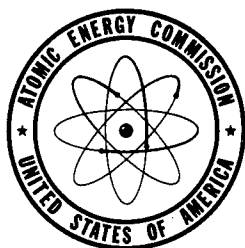UNITED STATES ATOMIC ENERGY COMMISSION

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VAPOR PRESSURE OF ZIRCONIUM TETRACHLORIDE BY MOLECULAR EFFUSION

By
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Ames Laboratory

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CHEMISTRY

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VAPOR PRESSURE OF ZIRCONIUM TETRACHLORIDE

BY MOLECULAR EFFUSION [1]

by

James M. Scarborough and Wm. K. Plucknett

From the Department of Chemistry
Iowa State College

I. ABSTRACT

Briefly, the methods of determining low vapor pressures have been reviewed. Emphasis has been placed on molecular effusion, including a theoretical discussion and the subsequent application of molecular beams to the determination of vapor pressure. The problems met in the preparation, purification and handling of anhydrous zirconium tetra-chloride have been discussed. Vapor pressure measurements on zirconium tetrachloride have been made over a temperature range of fifty degrees, 70° C. to 120° C., and the mean molar heat of sublimation for this temperature range has been calculated. The value of 20.3 kcal. per mole obtained is not unreasonable in view of the fact that values for the same quantity determined by other investigators in the temperature range of 239° C. to 346° C. is reported to be 24.4 kcal. per mole.

II. INTRODUCTION

Recently there has developed a great demand for the separation of zirconium and hafnium. Several of the earlier proposals for the separation were based upon differences in the vapor pressures of the zirconium and hafnium tetrachlorides. Consequently an accurate determination of the vapor pressure of these zirconium and hafnium halides over a considerable temperature range was desirable.

This work deals with the vapor pressure of zirconium tetrachloride at temperatures below 120° C. where the pressures were estimated to be in the range of 10^{-2} to 10^{-5} mm. of mercury. A review of the methods of determining pressures in this range indicate that the methods involving molecular effusion are remarkably applicable.

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[1] This paper is based on an M.S. thesis by J. M. Scarborough, December, 1950.

III. REVIEW OF THE LITERATURE

Numerous methods for the determination of low vapor pressures are described in the literature. Among these methods should be mentioned the hot wire manometer (1); several special forms of Walker's dynamic method (2); Knudsen's molecular effusion (3); the Knudsen gauge (4); the quartz fiber suggested by Langmuir (5) and used by Haber and Kerschbaum (6). Later, in 1923, Coolidge (7) used a modified Langmuir method. Other methods include the ionization gauge (8) and an improved optical lever manometer (9). In reviewing these various methods it seemed that the method based upon the work of Knudsen offers as convenient and as reliable a means as any of the other methods for the determination of low vapor pressures. Since the application of the theory of molecular effusion by Knudsen to the determination of the vapor pressure of mercury in 1909, there have been many adaptations and refinements of his method.

Knudsen's apparatus consisted of a glass tube separated into two compartments by a glass partition, having a small aperture in the center. Mercury was placed in the lower compartment where it was maintained at constant temperature. The other compartment was kept cool and was evacuated; mercury vapor flowed through the hole in the partition and was condensed in the cool portion of the tube. From the weight, G, in grams of mercury that condensed in a given time, it was shown from the kinetic theory that the difference in pressure in the two compartments was given by,

$$p - p' = (w_1 + w_2) \cdot G \ / \ t \sqrt{\rho}$$

where $w_1 + w_2$ is the resistance offered to passage of the vapor by the hole and the tube, where w_1 is given by,

$$w_1 = \sqrt{2\pi}/A,$$

in which A is the area of the hole. The resistance of the tube, w_2, is given by,

$$w_2 = (3/8) \cdot (\pi/2)^{1/2} \cdot \int_0^L (\sigma_1/A_1^2) \ dL,$$

in which L is the distance from the aperture to the condensation point, σ_1 is the circumference of the tube, and A_1 is the cross sectional area of length, dL, of the tube. ρ is the density of the vapor at a pressure of one dyne per square centimeter and t is time in seconds required for the weight, G, to condense.

Egerton (10,11) successfully used Knudsen's method to determine the vapor pressures of zinc, cadmium and mercury in 1917 and again in 1923 with a slight modification to determine the vapor pressure of lead. A modified Knudsen method was again used by Langmuir (12) and by Langmuir and Mackay (13) for the vapor pressure of electrically heated filaments; and by Pilling (14) for the vapor pressure of calcium. Swan and Mack (15) determined the vapor pressure of several organic crystals by an effusion method with inovations of both Knudsen and Pilling, and the vapor pressure of sodium was determined by Rodebush and DeVries (16) by the simple Knudsen method.

Molecular effusion methods have found application in fields other than the direct determination of vapor pressure. For example Stern (17) applied molecular effusion methods to produce molecular or atomic beams, the behaviors of which were studied in electric and magnetic fields. Effusion methods have been used to study the thermal dissociation of iodine and bromine (18); to determine the heats of formation of molecular hydrogen (19) and of molecular oxygen (20), to determine molecular weights of saturated vapors (21); and to study the mechanisms of homogeneous gas reactions (22).

No references appear in the literature on the vapor pressure of zirconium tetrachloride in the range of one millimeter of mercury or less. However, mention should be made of the work done covering the higher pressure region. Rahlfs and Fischer (23), using a null point manometer which utilized molten tin as the manometric fluid, investigated the sublimation pressures of zirconium tetrachloride over the temperature range from 262° C. to 334° C. Hoping to improve these measurements, Fischer, Gewehr and Wingchen (24) developed another null method. Their apparatus utilized a long evacuated quartz tube containing a molten pool of tin at its base and a small molybdenum cup suspended on a linen string arrangement attached to the top of the tube. The sample investigated was sublimed into the cup, and the cup was lowered by a windlass system into the pool of molten tin. The position of the cup was adjusted to a null point, previously determined, by applying external gas pressure to the system. At the null point, then, the vapor pressure of the compound inside the cup was equal to the external gas pressure. More recently Stock (25) has determined values from 246° C. to 337° C. using carefully purified material and utilizing a null point isoteniscope method. Here again, molten tin was used as the manometric liquid. The results of this work have been further verified and extended over a greater temperature range by Kuhn, Ryon and Palko (26).

IV. THEORY

Consider a vessel containing a solid with vapor in complete equilibrium with that solid. Suppose one of the walls of this vessel contains a small hole with a diameter less than the mean free path of the vapor molecules in the container. According to the classical theory a number of molecules will issue from the orifice independently of each other in the form of a molecular stream. The number of molecules effusing from this orifice is equal to the number of molecules striking an equivalent area on the wall of the container; furthermore, each of these molecules will move with the velocity it had as it approached the orifice. In order that equilibrium be maintained in the vessel this independent movement of molecules through the orifice must be slow enough to permit evaporation or sublimation and molecular chaos to cancel out the effects of the loss of these individual molecules. If the passage of molecules through the aperture is such that the equilibrium of vapor and solid is not disturbed, the mass motion of the vapor is zero; if the aperture is thin-edged, it can then be assumed that the effusion of the molecules through the orifice is the same as their flow across any small plane area of equal size drawn in the body of the vapor.

Therefore let us consider a small plane of area, S, drawn anywhere in a mass of gas that is in complete equilibrium. We shall consider those molecules that cross toward one side only, since we shall be concerned with effusion of molecules through an orifice into a high vacuum. Out of n molecules per unit volume, $4\pi nBv^2 \cdot e^{-\beta^2 v^2} dv$ are moving with speeds in a given velocity range, dv, where v is velocity and B and β are constants derived from the kinetic theory (27) and given by the expressions below:

$$B = \beta^3/\pi^{3/2}$$

and

$$\beta = 2/\bar{v}\sqrt{\pi},$$

where $\bar{v}$ is the average velocity. Since they are moving equally in all directions the fraction $d\omega/4\pi$ of them are moving in a direction lying in a given solid angle, $d\omega$, whose axis makes an angle, Θ, with the normal to S. As many of these molecules will cross S during a given time, dt, as lie at the beginning of dt within a cylinder standing an S and having a slant height, v dt, and therefore, a volume $Sv \cdot dt \cdot \cos\Theta$. Hence, the number so crossing is the number in the cylinder at the beginning of dt, or

$$4\pi nBv^2 e^{-\beta^2 v^2} dv \cdot (d\omega/4\pi) \cdot Sv \cdot dt \cdot \cos\Theta.$$

Dividing this expression by S and by dt, we have, accordingly,

$$d^2q = nBv^3 \cdot e^{-\beta^2 v^2} \cos\theta \cdot dv \cdot d\omega,$$

the number of molecules crossing S per unit area per second with veloci-
ties lying in the range dv in magnitude and in the solid angle d of
direction. The number of molecules, dq, in the velocity range from $0 \to \infty$
in the solid angle, $d\omega$, is given by,

$$dq = nB \cdot \cos\theta \cdot d\omega \int_0^\infty v^3 e^{-\beta^2 v^2} dv = (nB/2\beta^4)\cos\theta \cdot d\omega,$$

but $d\omega = 2\pi\sin\theta \cdot d\theta$. Therefore,

$$dq = (\pi nB \cdot \cos\theta/\beta^4) \sin\theta d\theta.$$

Then the number of molecules, q, per unit area of orifice going through
the collimator per second is,

$$q = \int_0^\theta (\pi nB \cdot \cos\theta/\beta^4)\sin\theta \cdot d\theta = (nB\pi/2\beta^4)\sin^2\theta.$$

Let N^V equal the number of molecules per second striking a target
placed above the collimator. Then,

$$N^V = qa = (nB\pi a \cdot \sin^2\theta/2\beta^4),$$

where a is the area of the orifice. Substituting $\beta^3/\pi^{3/2}$
for B and $2/\pi^{1/2} \bar{v}$ for β,

$$N^V = (n\bar{v}a/4)\sin^2\theta$$

The number of moles, N, effusing per second may be obtained by div-
iding N^V by Avogadro's number, N_a, i.e.

$$N^V = (n\bar{v}a/4N_a)\sin^2\theta.$$

By definition

$$n/N_a = p/RT \qquad \text{and} \qquad \bar{v} = 2\sqrt{(2RT/\pi M}$$

where R is the molar gas constant and p is pressure in dynes per
square centimeter. If now, we let A equal the area of the collimator
in square centimeters,

$$\sin^2\theta = A/\left[\pi r^2(1 + \rho^2/r^2)\right]$$

where r is the distance from the orifice to the collimator in centi-
meters and ρ is the radius of the collimator in centimeters. Hence,

$$N = (pa/\sqrt{2\pi RTM}) \cdot \left[A/\pi r^2(1 + \rho^2/r^2)\right].$$

By making the substitution, $A = \pi \rho^2$, the above expression can be simplified to

$$N = (pa/ \sqrt{2\pi RTM}) \cdot \left\{ 1/ \left[1 + (r^2/\rho^2) \right] \right\}$$

or

$$p = \sqrt{2\pi RTM \cdot \left[1 + (r^2/\rho^2) \right]} \cdot N \cdot (1/a) \text{ dynes} / cm.^2$$

If w equals the weight in grams of material effusing through the orifice-collimator system, M is the molecular weight of the material, and t is the length of time in seconds for w to effuse, the number of moles effusing per second is given by

$$N = w/Mt.$$

The pressure of the vapor in the effusion vessel in millimeters of mercury is then given by

$$p = \frac{(2\pi R)^{1/2}(1 + r^2/\rho^2) \cdot 7.50 \times 10^{-4}}{a \sqrt{M}} \cdot \frac{w \cdot T^{1/2}}{t}.$$

Therefore, if we can determine N and if we know the geometry of the orifice-collimator system, the molecular weight of the vapor, and the other experimental values appearing in the expression for pressure, we can calculate the vapor pressure of a substance at a given temperature.

Two methods have been used to determine N or w as the case may be. The vapor effusing through the orifice-collimator system is collected on a platinum target cooled by liquid nitrogen, the amount of material collected being determined in two different ways:

1. Zirconium enriched with Zr^{95} was used to prepare the zirconium tetrachloride. The activity of the deposit collected on the target was then compared to a standard of known weight made up from the same sample of zirconium tetrachloride used in the pressure determinations.

2. The amount of zirconium tetrachloride collected on the platinum target was determined colorimetrically by placing the target and deposit in a given volume of one normal hydrochloric acid which dissolved the deposit giving a solution containing only the zirconium, the amount of which could be determined spectrophotometrically utilizing the zirconium-alizarin lake method.

V. EXPERIMENTAL

A. Apparatus

1. Apparatus for the preparation of zirconium tetrachloride

Although the size of the apparatus varied with the quantity of the chloride produced, the principle remained essentially the same. The apparatus consisted of a long pyrex tube, fitted at each end with a ground, standard taper joint. The tube was placed in an ordinary combustion furnace which was free to move the entire length of the tube. Purified zirconium oxide was introduced into one end of this tube, and this end was attached, by means of the standard taper joint to a source of anhydrous chlorine saturated with vapor from purified carbon tetrachloride. By means of a stopcock arrangement, helium could be passed into the train in place of the chlorine. The other end of the long tube was connected, by means of the other standard taper to a drying tube and sulfuric acid bubbler used to indicate rate of flow of gas. Zirconium tetrachloride was produced by passing the chlorine and carbon tetrachloride vapors over the oxide heated to about 300°C. The chloride condensed on the cold portion of the tube and when a sufficient amount was obtained it was resublimed several times in helium down the length of the long tube until it was deposited near the standard taper joint in that portion of the tube. Then the tube was sealed off on each side of the standard taper joint to give a small vial of zir-conium tetrachloride. The vial could then be transferred to a dry box and the sample removed through the standard taper joint. In a later modification of the method to produce smaller samples and to reduce the possibility of moisture coming into contact with the sample, this last standard taper joint was eliminated by merely seal-ing the smaller sample into a short portion of the tube which could then be broken in the dry box to remove the sample.

2. Apparatus for measurement of vapor pressure

Three types of apparatus were used. One type was employed in the method involving radioactive zirconium tetrachloride, and two similar types were utilized in the method involving the spectrophotometric analysis. The first type is shown in Figure 1. The large effusion chamber consists essentially of two sections of pyrex tubing three and one-half inches in diameter which join with a standard taper, G, Target holder, F, fits into the upper part of the effusion chamber by means of standard taper, H, which permits rotation of the targets, E, which are held in place with tin foil with holes for the targets as

VIEW SHOWING TARGET
ARRANGEMENT ON TARGET-HOLDER

VIEW   SHOWING BOTTOM
OF EFFUSION CHAMBER

TO VACUUM SYSTEM

GLASS WOOL

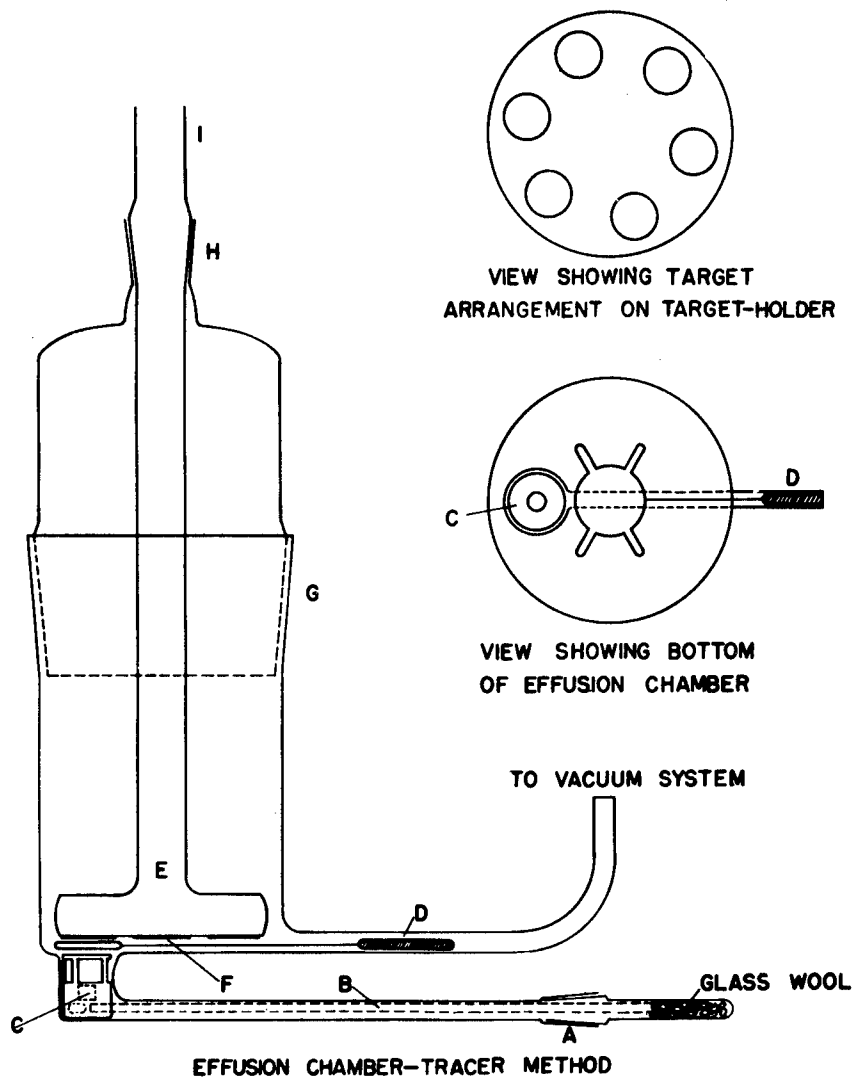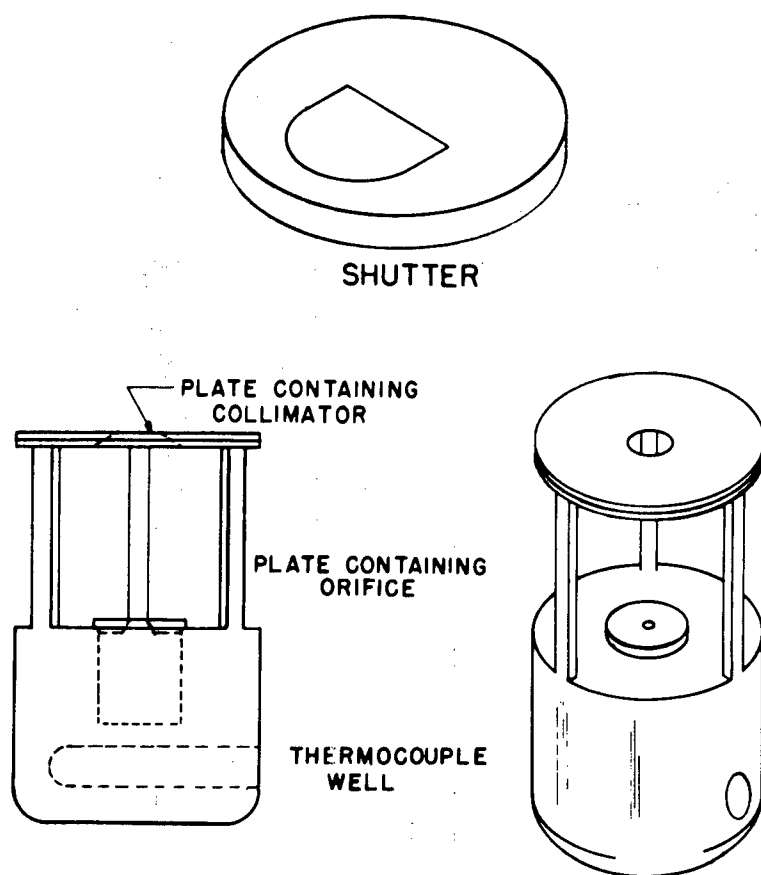EFFUSION CHAMBER—TRACER METHOD

Figure 1

shown in the figure. Radioactive zirconium tetrachloride is contained
in the effusion vessel, C, which is shown in detail in Figure 2. B
is a thermometer which may be introduced at joint, A, and D is a shutter
which may be operated by action of a magnet on the small piece of soft
iron attached to the shutter mechanism. A vapor pressure run can be
made by placing radioactive zirconium tetrachloride in the effusion
vessel, attaching the orifice and collimator and assembling the
apparatus as shown. After evacuation is complete and a good vacuum
can be maintained, the constant temperature bath may be raised around
C and the heating begun. Liquid nitrogen is then added to target
holder, F. The shutter which has been closed during the preceding
operations can now be opened and the actual run started. At the end
of the desired period of time the shutter is closed and the target
holder rotated to bring a new target into position, after which the
shutter may again be opened and another run started. This procedure
is repeated until all six targets have been exposed. The liquid
nitrogen is removed and the heating bath lowered; the apparatus is
disassembled, the targets removed, their activity determined and the
appropriate calculations made for vapor pressure.

With the second type of apparatus shown in Figure 3, the pro-
cedure is simplified by exposing only one target per run and determining
the amount of deposit colorimetrically. This one target, G, is wired
into place on cold finger, F, a copper-constantan thermocouple replaces
the thermometer, and a new type of shutter, E, shown in Figure 2 is
used. The thermocouple leads are sealed through a capillary tube, A,
with apiezon wax; connection to the effusion chamber is made with
standard taper, B. K is attached to high vacuum source.

Figure 4 shows the third type of apparatus which is essentially
the same as that previously described with the exception that several
target exposures may be made with one loading of the effusion vessel.
This multiple exposure method is made possible by means of a windlass
system made up of the two winders, J, to which steel wires, H, are
attached. These wires are fastened to the ends of a platinum strip
five inches long and three quarters of an inch wide which is free to
move over the flattened surface of cold finger, F, as shown in the
figure; tension on the wire, H, is adjusted so that target strip, G,
fits snugly around the cold finger. Here the exposures are made on the
various targets by turning the winders in the appropriate directions.
At the end of a run the target strip is removed and various target
deposits determined colorimetrically.

3. Effusion vessel

The effusion vessel, Figure 2, was made of nickel and consisted
of three basic parts; the oven, the orifice and the collimator. In
the section containing the oven was also located the thermocouple well

SHUTTER

PLATE CONTAINING
COLLIMATOR

PLATE CONTAINING
ORIFICE

THERMOCOUPLE
WELL

EFFUSION VESSEL AND
SHUTTER—COLORIMETRIC METHOD

Figure 2

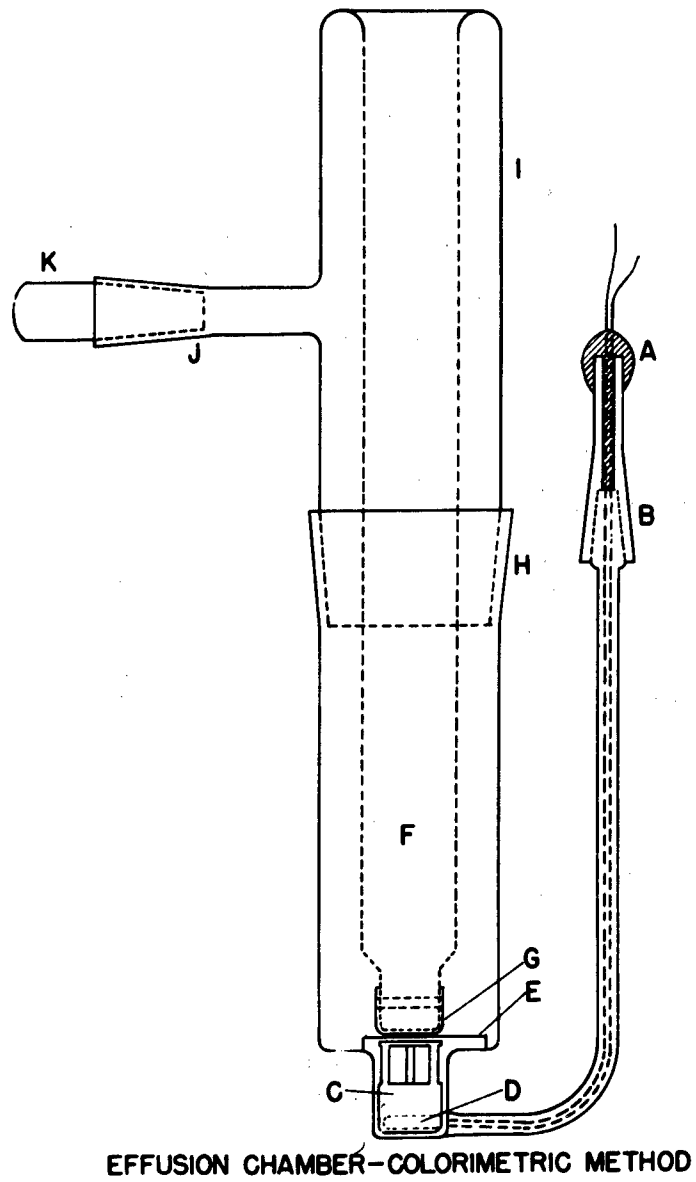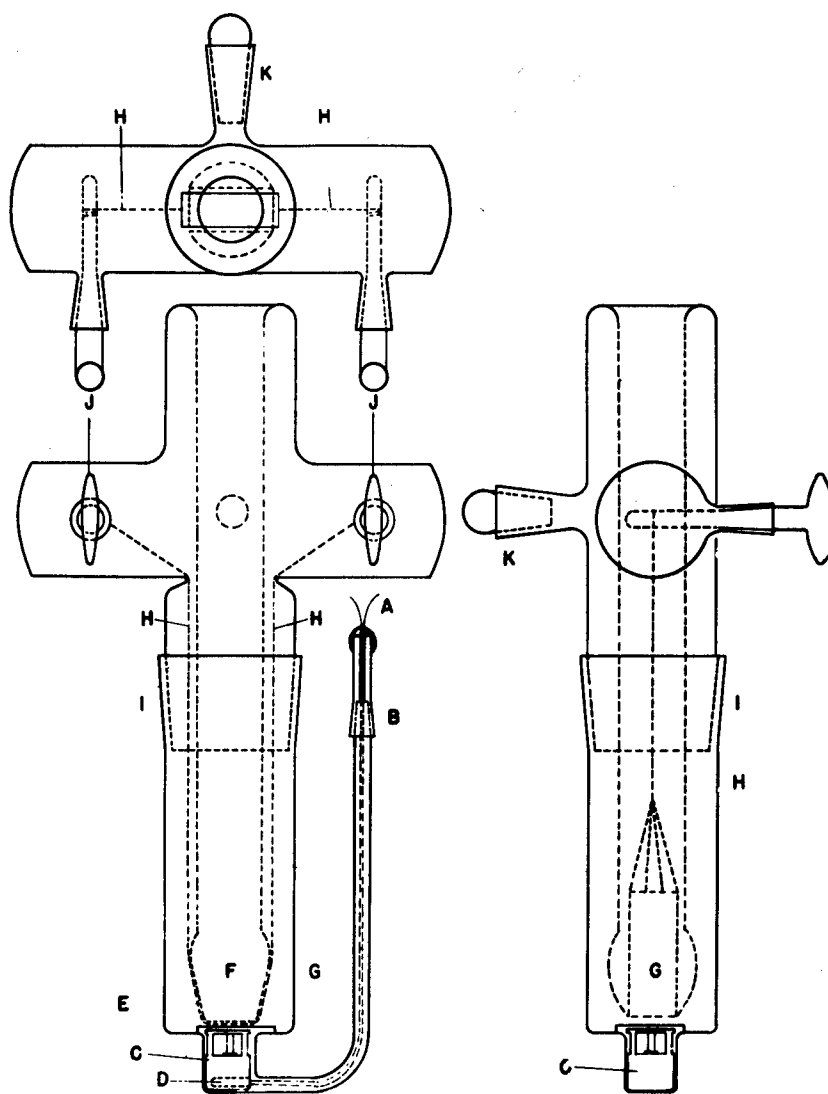EFFUSION CHAMBER-COLORIMETRIC METHOD

Figure 3

EFFUSION CHAMBER — MULTIPLE TARGET METHOD

Figure 4

and the supports for the collimator piece. The orifice was located in
the center of a thin nickel plate which fit over the oven and similarly
the collimator slot was located in the center of a larger nickel plate
fitting into the circular support on the oven so that the orifice and
the collimator slots were concentric. The surfaces of the orifice and
the collimator were polished until the apertures were thin edged. A
linear comparator was used to measure the diameter of the orifice and
the collimator slots, the value recorded being the average of a number
of readings. The shutter which was made of steel which is also shown
in Figure 2 fit over the top of the effusion vessel and could be oper-
ated with a small magnet.

4. Vacuum system

The vacuum system is shown schematically in Figure 5. Pressure
measurements were made with an ionization gauge, calibrated with the
apparatus completely assembled in the same manner and procedure as in
the vapor pressure runs.

5. Constant temperature bath

The heating bath consisted of medium weight mineral oil with
heaters regulated by a merc-to-merc micro thermoregulator, which kept
the temperature constant to $\pm$ 0.10° C. at 120° C. The temperature of
the bath was measured with a calibrated mercury thermometer, and the
temperature of the effusion vessel was measured in some cases, as
indicated, with a mercury thermometer and in other cases with a copper-
constantan thermocouple. The actual temperature of the zirconium
tetrachloride in the effusion vessel was measured in dummy runs using
the copper-constantan thermocouple immersed in the substance under the
operating conditions. In all cases the time lag between the temperature
of the bath and the temperature of the charge in the effusion vessel
was short. Consequently, a large number of runs were made which relied
only upon the temperature of the bath in order to simplify the procedure.

A vacuum-tight seal for the thermocouple leads was made by passing
the wires through a capillary tube one and one-half inches long which
had at one end a standard taper joint for sealing to the effusion
chamber. Hot Apiezon wax was poured in around the thermocouple leads
in the capillary tubing and allowed to solidify.

B.   Experimental Procedure

1. Preparation of samples

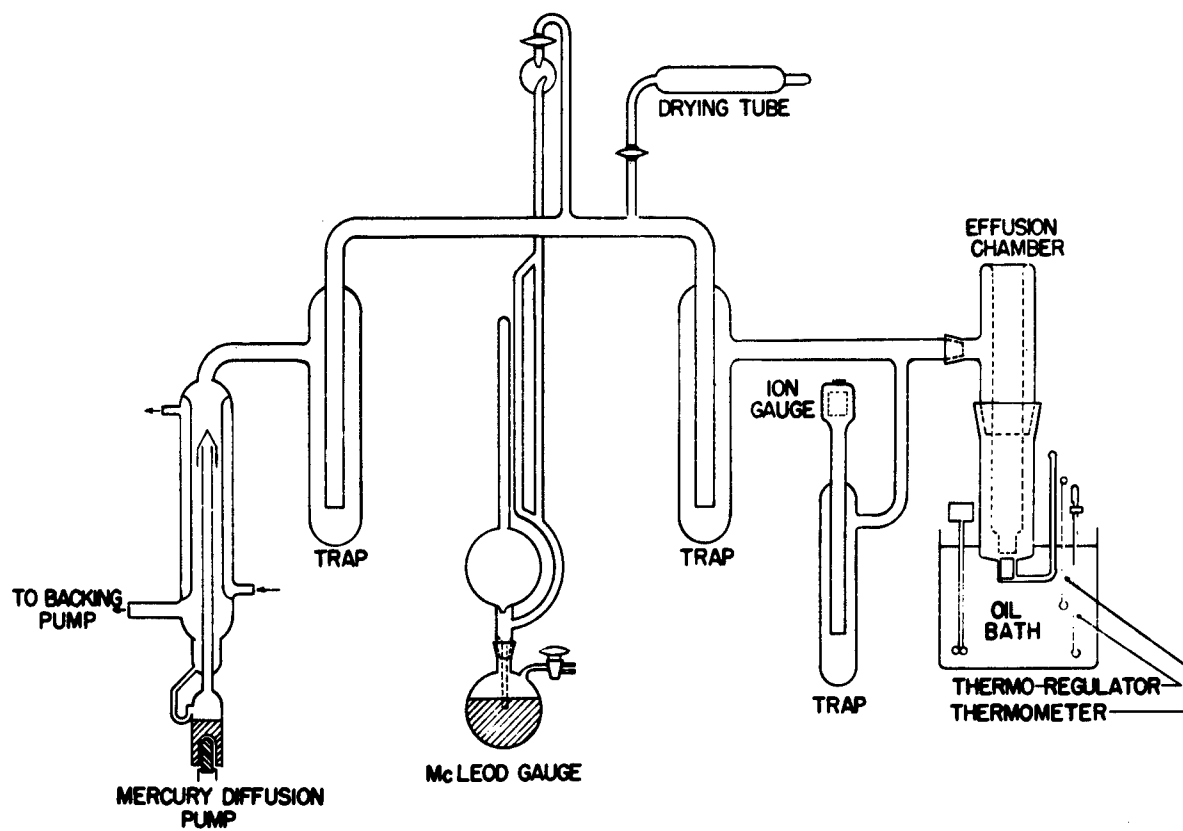Radioactive zirconium tetrachloride was prepared by adding seven

Figure 5

milliliters of carrier-free active Zr^{95} solution in the form of the
oxalate complex to five milliliters of a solution of zirconyl chloride
containing 0.0268 grams of zirconium per milliliter. The solution was
then diluted to 100.0 milliliters and a 25 λ aliquot was withdrawn and
evaporated on a platinum disk to make a counting standard. Ignoring
the weight of the Zr^{95} added the weight of the zirconium on the disk
was 0.026 milligrams. This sample provided a constant record of the
specific activity of the zirconium tetrachloride during the course of
the experiment. The remainder of the solution was converted to zir-
conium hydroxide, washed and filtered and ignited to the oxide. The
oxide was then converted to the tetrachloride by heating it in a
stream of chlorine saturated with carbon tetrachloride vapor. The
chloride was then sublimed several times and the final sample sealed
off in a portion of the tube containing a ground glass joint which
could be opened to remove the zirconium tetrachloride. Proper precau-
tions were taken against the high beta and gamma activities.

Preparation of inactive zirconium tetrachloride was achieved by
dissolving impure zirconium tetrachloride in a solution of 1:1 hydro-
chloric acid. The solution was allowed to evaporate until crystals
of zirconyl chloride were formed. These crystals were removed and
washed in a 1:1 mixture of concentrated hydrochloric acid and ethyl
alcohol. After a thorough washing the crystals were redissolved and the
recrystallization process repeated three more times. The final crystals
produced were free of impurities except for spectrographic traces of
boron, copper, iron, sodium (strong), magnesium, and titanium. The
hafnium content was 1.42%. This purified zirconyl chloride was dis-
solved in distilled water and ammonium hydroxide added until a precipi-
tate of zirconium hydroxide was formed. After being washed, the
hydroxide was dryed and then ignited at 300° C. for several hours.
The resulting oxide was converted to the tetrachloride by passing dry
chlorine saturated with purified carbon tetrachloride vapors over the
oxide at 300° C. Without being exposed to the air, the zirconium
tetrachloride thus formed was resublimed several times and finally
sealed off in a portion of the pyrex glass tubing containing a standard
taper joint. This zirconium tetrachloride yet unexposed to air was
stored in a desiccator until used. Precautions were taken to eliminate
the possibility of moisture coming into contact with the zirconium
tetrachloride; the container was never opened except in the dry box.
The procedure was later modified to produce smaller samples which
would be used only once; these samples were sealed in short portions of
the sublimation tube without the standard taper joint. It was neces-
sary to break this tube inside the dry box to remove the sample.

The above preparations contained varying amounts of hafnium. In
the meantime, however, a method was developed by Hansen (28) for

separating zirconium and hafnium, and this process was used to prepare
hafnium-free oxide which could then be converted to the tetrachloride.
Two hundred grams of commercial zirconium tetrachloride containing more
than 2% hafnium were dissolved in one liter of cold methanol and fil-
tered. This solution was then diluted to give 1.2 liters total volume
and passed through a pyrex column 2 feet high and 2 inches in diameter
containing 400 grams of purified, freshly activated silica gel through
which 500 milliliters of pure methanol had previously been run. The
first 700 milliliters of the effluent were added to an equal volume of
water and made basic by addition of ammonia. The hydroxide formed
was then washed and filtered and then dissolved in concentrated hydro-
chloric acid. This solution was then filtered and allowed to evaporate
until crystals of zirconyl chloride formed. These crystals were washed
in a I:I mixture of concentrated hydrochloric acid and ethyl alcohol
several times and dried. This dry zirconyl chloride was then redis-
solved and the resulting solution filtered; zirconium hydroxide was
again precipitated, washed, filtered, dried, and ignited at 300° C. The
resulting oxide was then chlorinated in the manner previously described.
In the process chlorination and sublimation was repeated for each small
sample prepared. The hafnium content of all zirconium tetrachloride
prepared in this manner was less than 0.05% by weight with traces of
aluminum, boron calcium, copper, magnesium, nickel, and titanium;
silicon was present to the extent of not more than 0.05%.

2. Vapor pressure measurements

Due to the fact that radioactive Zr^{95} became unavailable shortly
after experimentation was begun, the data obtained by this method were
limited and probably not reliable. Errors arose from scattering of the
molecular beam because the distance between orifice and target was too
great and because the effusion vessel did not fit securely into the
well (C in Figure 1) of the effusion chamber, permitting the direction
of the beam to change erratically. Even though the data obtained gave
only an order of magnitude indication of pressure, the method should
give reliable results with the proper design and operation of the equip-
ment; consequently, only a brief description of the method will be
given here.

Radioactive zirconium tetrachloride, prepared in the manner
previously described, was placed in the crucible, C, Figure 1. With
the orifice and collimator in place, C was placed in the effusion
chamber which was then assembled as shown in the figure and attached
to the vacuum system. Evacuation of the system was carried out rapidly,
the constant temperature bath moved into place and heating begun. When
a vacuum of better than 10^{-4} millimeters of mercury was obtained, liquid
nitrogen was introduced into target holder, F. When the pressure of

the system reached the range of 10^{-5} millimeters and the desired temperature was attained, the shutter, D, was opened and the time noted. At intervals of about one-half hour, the pressure of the system was checked and the temperature noted on thermometer, B. At the end of a period of from two to ten hours the shutter was closed and the target holder rotated to expose a new target. If a new temperature was desired the thermostat could be adjusted at that time. The process was repeated until all six targets were exposed. With the shutter closed and the effusion vessel cooled to room temperature, dry helium was passed into the system, and the liquid nitrogen remaining in F was removed. While F was still at a temperature below freezing the effusion chamber was taken apart at G and moisture allowed to collect on the targets to hydrolize the zirconium tetrachloride deposited to non-volatile zirconyl chloride. The targets were then removed and placed in small aluminum cups for counting purposes, and the activity of the target deposits determined. This activity was compared to the activity of the standard sample, previously described, permitting the calculation of the number of moles of zirconium tetrachloride, effusing per second and, hence, the vapor pressure.

The amount of radioactive niobium formed by the decay of Zr^{95} was considered negligible in its effect on the vapor pressure of zirconium tetrachloride, and its activity filtered out with an aluminum absorber in the counting procedure.

Since the data which were obtained using inactive zirconium are reported here, a detailed description of the methods used will be given. All operations involving transfer of zirconium tetrachloride were performed at first in a dry box in an atmosphere of dry nitrogen. In the earlier part of the work the effusion vessel was loaded for each run from a vial containing several grams of the chloride, each vial being used over a period of several weeks. Data obtained from these measurements were somewhat erratic and indicated that moisture was in some way coming into contact with the zirconium tetrachloride during manipulation. Consequently extreme precautions to eliminate this possible source of error were made. All gaskets and connections on the dry box were carefully resealed, and dry helium, instead of nitrogen, was supplied to the box from cylinders after first passing it through a magnesium perchlorate drying tube and then through a double liquid nitrogen trap. After passing through the liquid nitrogen trap the helium was heated to room temperature by passing it through a hot pyrex tube. The outlet on the dry box for the helium was protected from moisture by a magnesium perchlorate drying tube and a concentrated sulfuric acid bubbler. The main working section of the dry box was protected by a smaller loading compartment or air lock. No sample of zirconium tetrachloride was opened for at least one and one-half hours after the apparatus was placed in the

working compartment. The effusion vessel was loaded and the apparatus
assembled as rapidly as possible and the equipment removed from the box.

The following step-wise procedure was adopted for each vapor
pressure run.

(a) The platinum target was attached to the cold finger with
steel wire.

(b) All pieces of glassware, the effusion vessel, the ori-
fice, the collimator and the shutter were washed and then baked in
a drying oven at 125° C. for several hours.

(c) All equipment was placed in the loading compartment of
the dry box and the flow of helium started. With the outside
door closed the apparatus was shifted to the working compartment.

(d) After at least two hours the standard taper joints were
greased with Apiezon "N" grease, about 50 milligrams of zirconium
tetrachloride, from one of the small sealed tubes stored in the
dry box, were placed in the effusion vessel.

(e) With the orifice and collimator in place on the effusion
vessel, the apparatus was assembled as shown in Figures 3 or 4.

(f) Cap, K, was removed and effusion chamber quickly attached
to the vacuum system and evacuation begun.

(g) The heating bath was raised around C.

(h) When the pressure of the system reached 5×10^{-5} milli-
meters of mercury, liquid nitrogen was introduced into cold finger,
F.

(i) As soon as the effusion vessel reached the desired
temperature, the shutter was opened, the time and the pressure of
the vacuum system noted.

(j) The temperature and the pressure were noted periodically
during the vapor pressure run. Liquid nitrogen was kept in F
throughout the run.

(k) At the end of the run the shutter was closed, the heating
bath removed and C cooled with an ice bath.

(l) The excess liquid nitrogen in F was removed and the
vacuum released.

(m) Cold finger, F, then quickly removed while still cold
enough to permit moisture to condense on the target to hydrolyze
the chloride to zirconyl chloride. The target was then removed
and placed immediately in a ten millimeter volumetric flask con-
taining two milliliters of one normal hydrochloric acid.

(n) The resulting solution which contained all the zirconium
deposited on the target by the molecular beam was then set aside
for analysis as described in the next part of this section.

A slight modification of the above procedure was necessary when
the multiple target apparatus shown in Figure 3 was used, that modifi-
cation being the operation of the target strip as described under part

1 of this section. At the end of the run it was also necessary to cut the target strip into the individual targets to place them in volumetric flasks as described above.

3. Analysis of the target solutions

Of the methods for determining very small quantities of zirconium, that of Liebhafsky and Winslow (29) involving the zirconium-alizarin lake appeared to be most adaptable to this work. However, in order to get the desired sensitivity in the range of ten micrograms per milliliter or less, it was necessary to modify their procedure considerably; the detailed procedure which was strictly followed in every determination is given below.

Two milliliters of solution to be analyzed were placed in a ten milliliter volumetric flask. Exactly 0.5 milliliter of 0.125% alizarin solution in ethyl alcohol was added, after which concentrated ammonium hydroxide was added until the solution was basic. The mixture was then allowed to stand for two minutes and one drop of seven normal hydrochloric acid added; one normal hydrochloric acid was then added until the mixture was slightly acid. The mixture was diluted to a total volume of ten milliliters with 95% ethyl alcohol immediately. After standing for four hours, the solution was placed in one cell of a Beckman spectrophotometer, and the optical density determined by comparison to a similar cell containing a solution prepared as above using one normal hydrochloric acid instead of the zirconium solution. The calibration curves shown in Figures 6 and 7 were prepared exactly in this manner using solutions from a carefully prepared standard solution of zirconyl chloride. The only variation in the analysis of the target solution and the standard solutions was that the platinum target of negligible volume remains in the volumetric flask containing the target solution. Control solutions prepared from standards were run along with the target solutions. Optical density measurements were reproducible in each determination to three significant figures on the standards. Consequently this sensitivity was assumed to hold for the target solutions.

VI. RESULTS

Once the necessary precautions were taken to eliminate any possible contact of the sample with air containing water vapor the values for the vapor pressure became reproducible. It was necessary to use zirconium tetrachloride which contained varying amounts of hafnium in the earlier experiments, but with the development of a method to separate zirconium and hafnium it was finally possible to produce hafnium-free zirconium tetrachloride.
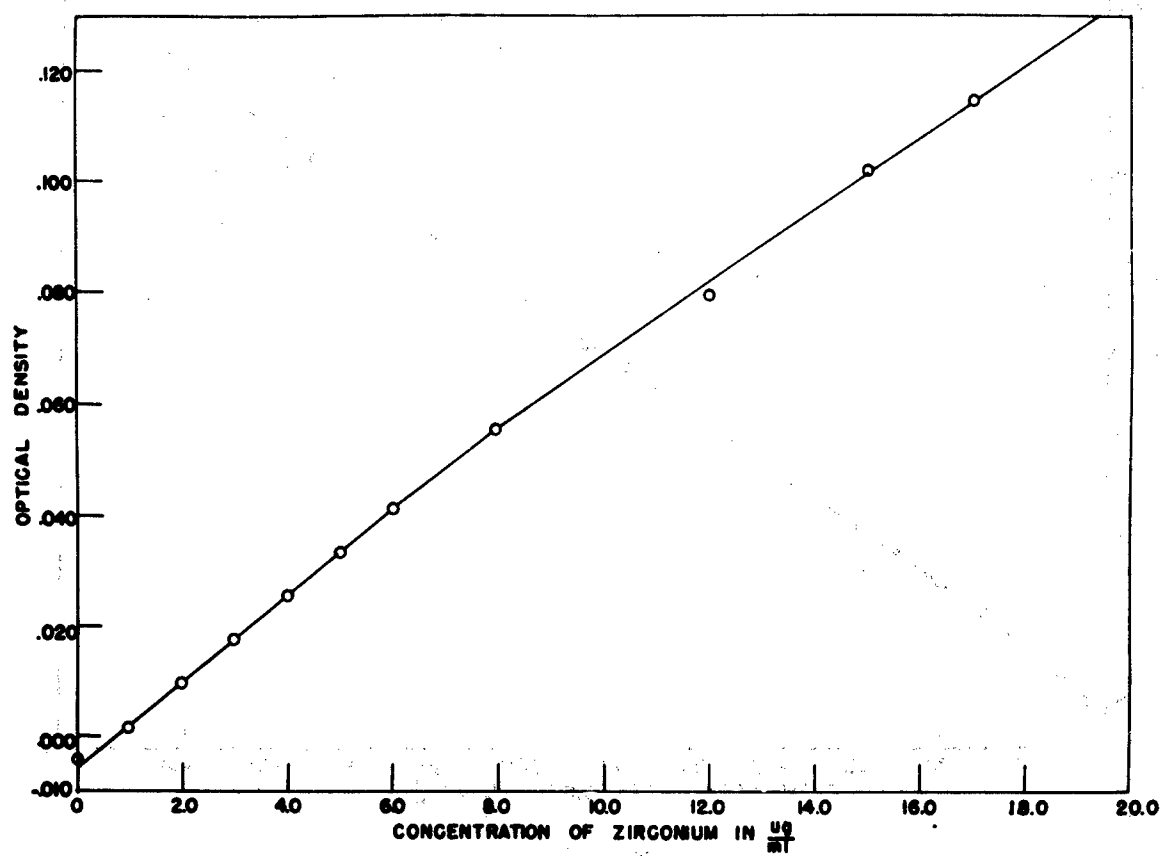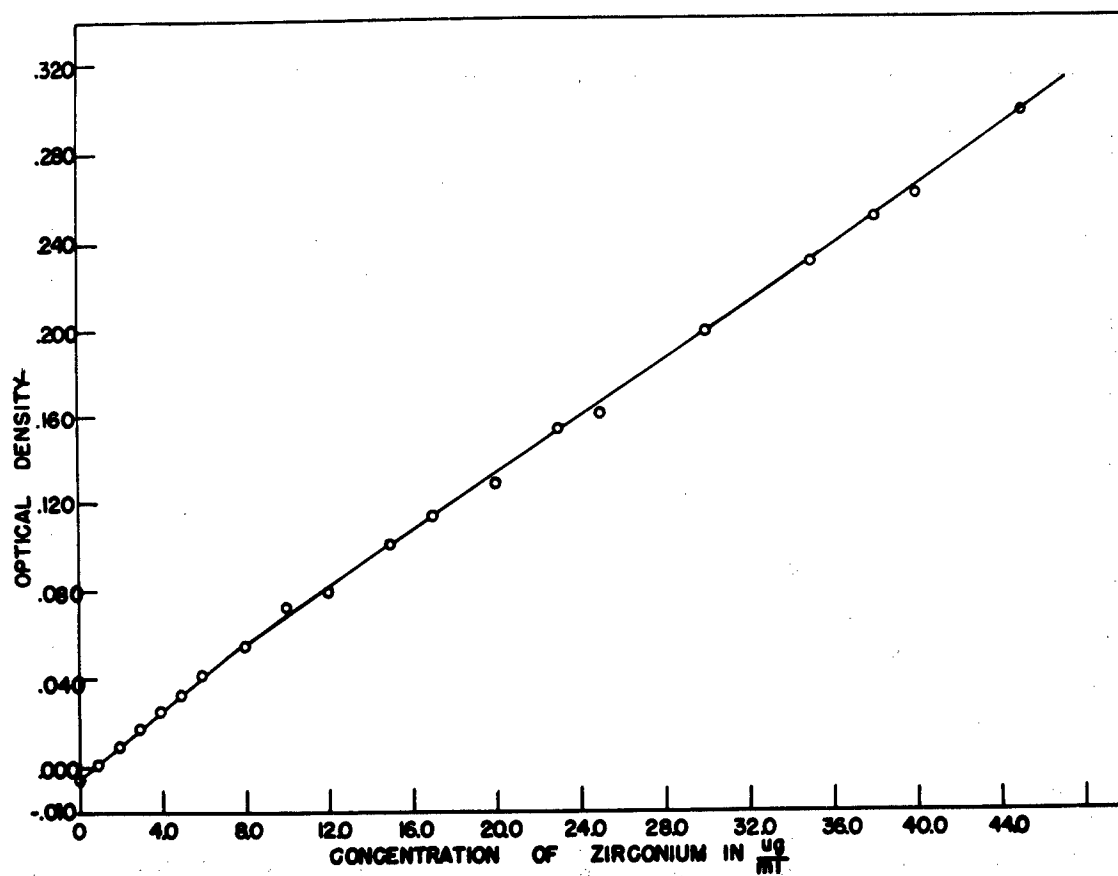
Figure 6

Figure 7

Utilizing the expression derived under section IV it was possible to calculate the vapor pressure of zirconium tetrachloride at various temperatures. The physical constants pertinent to the calculations are given in Table I.

Symbol	Description	Value
a	Area of orifice in sq. cm.	0.0106
A	Area of collimator in sq. cm.	0.0925
ρ	Radius of collimator in cm.	0.1716
r	Distance between orifice and collimator in cm.	1.70
R	Molar gas constant in ergs deg.$^{-1}$ mole^{-1}.	$8.314 \cdot 10^7$
M	Molecular weight of vapor	233.1
--	Factor to convert dynes cm.$^{-2}$ to millimeters of mercury	$7.50 \cdot 10^4$

TABLE I
Physical Constants

By grouping all of these constants the expression for the vapor pressure simplifies to

$$P_{mm.} = k(w\ T^{1/2}/t) = 1.05 \times 10^4\ (w\ T^{1/2}/t).$$

Table II summarizes the variable experimental data necessary for the calculations, and Figure 8 shows a plot of the logarithm of the vapor pressure versus the reciprocal of the absolute temperature. The best straight line that could be drawn through the points was drawn, and the average mean deviation of the points from the straight line was calculated to be $\pm$ 5%. The equation of the straight line is given by,

$$\log P_{mm.} = -(4438/T) + 8.937,$$

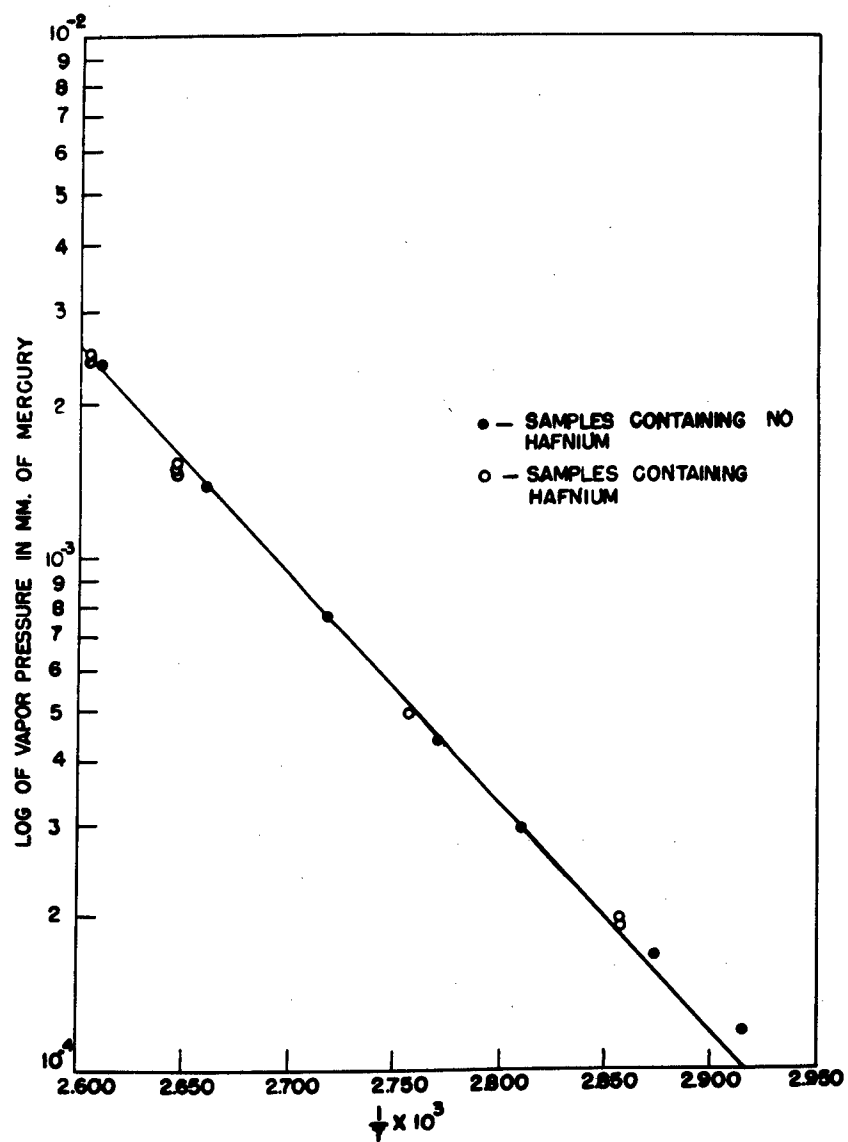and the mean molar heat of sublimation was calculated to be 20.3 $\pm$ 1.0 kcal. per mole.

Figure 8

Target No.	% Hf By Weight	$T^{o}k$	$\sqrt{T^{o}k}$	$t_{sec.}$ x 10^{-3}	w_{ug}	$P_{mm.}$x 10^{4}
1	3.04	350	18.71	24.6	24.0	1.92
2	2.82	"	"	21.6	21.9	1.99
3	3.05	363	19.05	10.8	26.5	4.92
4	"	"	"	"	"	"
5	2.65	"	"	18.3	44.8	4.98
6	2.95	378	19.44	10.8	79.5	15.0
7	3.04	"	"	7.2	51.5	14.5
8	"	"	"	"	53.0	15.0
9	"	"	"	"	54.1	15.3
10	?	384	19.60	"	85.2	24.3
11	"	"	"	"	86.8	24.8
12	"	"	"	"	87.7	25.0
13	<0.05	343	18.52	21.6	13.2	1.19
14	"	"	"	"	"	"
15	"	348	18.65	18.0	15.3	1.67
16	"	356	18.87	7.2	10.7	2.95
17	"	361	19.00	"	15.8	4.38
18	"	368	19.18	10.8	41.3	7.70
19	"	376	19.39	7.2	49.5	13.9
20	"	383	19.57	18.0	209.6	23.9

TABLE II
Experimental Variables

VII. DISCUSSION

The problems of preparing pure zirconium tetrachloride and of preventing contact with water vapor of the atmosphere during experimental operations have made this work unusually long and tedious in view of the relatively simple operations involved. Apparently the most minute amounts of water vapor coming into contact with the zirconium tetrachloride hydrolyzed surface layers of the small particles to form the non-volatile zirconyl chloride. The formation of this outside non-volatile layer resulted in erratic values for the vapor pressure and in some cases reduced pressures to practically zero. However, with the introduction of extreme precautions taken in the dry box procedure and with the use of individual samples for each run, the effect of moisture was apparently eliminated and a degree of consistency was attained.

The method appears to be readily applicable to other compounds having low vapor pressures, especially those that are stable and easy to handle. It has been shown that small quantities in the range of several micrograms of zirconium tetrachloride collected on the targets could be readily determined; this method of determining the amount of material effusing through an orifice-collimator system could easily be extended to many other elements or compounds that are readily determined colorimetrically in trace amounts.

Where a colorimetric procedure is not applicable one might apply a radioactive tracer technique or a gravimetric method involving the simple weighing of the target deposit. The radioactive technique is especially applicable where quantities are limited or where very low vapor pressures are involved. From this latter point of view it is interesting to note that as few as several thousand radioactive molecules may be detected, even when contained in sizable samples.

Of the methods for determining low pressures, molecular effusion offers the most direct approach, especially where the simple Knudsen method, which relies on determining the total quantity of material effusing through an orifice into high vacuum, can be used. The usual procedure in the case of the Knudsen method is to determine the loss in weight of the effusion vessel in a given time. To obtain accurate results from such a method requires elaborate weighing methods and is usually time-consuming in that weighable quantities must effuse through the small orifice. The collimated beam method is to be preferred in many cases in that it offers a rapid, reliable method which involves only ordinary laboratory equipment.

VIII. SUMMARY AND CONCLUSIONS

Briefly, the methods of determining low vapor pressures have been reviewed. Emphasis has been placed on molecular effusion, including a theoretical discussion and the subsequent application of molecular beams to the determination of vapor pressure. The problems met in the preparation, purification and handling of anhydrous zirconium tetra-chloride have been discussed. Vapor pressure measurements on zirconium tetrachloride have been made over a temperature range of fifty degrees, 70° C. to 120° C., and the mean molar heat of sublimation for this temperature range has been calculated. The value of 20.3 kcal. per mole obtained is not unreasonable in view of the fact that values for the same quantity determined by other investigators in the temperature range of 239° C. to 346° C. is reported to be 24.4 kcal. per mole.

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X. ACKNOWLEDGMENTS

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